

# Energetics of Mechanism of OH-Propene Reaction at Low Pressures in Inert Atmosphere

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Received 5 September 1997; accepted 19 December 1997

**ABSTRACT:** MP2 calculations with full geometry optimizations were performed with a double- and a triple-zeta basis set to obtain the energy profile for reactions of propene + OH and ethene + OH at low pressures. In these conditions, the  $\beta$ -hydroxyalkyl radicals formed after OH addition to the alkene double bond may go through a rearrangement reaction to form easily identifiable aldehydes and ketones. The theoretical results obtained reproduce the available experimental data well and shed light on the mechanism of reactions characterized by negative activation energies. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 811–819, 1998

**Keywords:** hydroxyl radical; alkenes; atmospheric reactions; OH addition; reaction mechanism

## Introduction

It is widely accepted that the most common initial reaction of hydrocarbons in the atmosphere is the attack by an OH radical.<sup>1</sup> For unsaturated hydrocarbons, the latter results in the addi-

tion of OH to one of the carbon atoms of the double bond to form a  $\beta$ -hydroxyalkyl adduct,  $[R-OH]^*$ ,



followed by either decomposition or collisional stabilization.

In the case of alkenes, this reaction is characterized by a reaction constant that decreases with increasing temperature, yielding an Arrhenius

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Contract/grant sponsor: Instituto Mexicano del Petróleo;  
contract/grant number FIES-95-97-VI

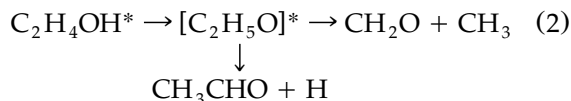
curve with a negative slope, thus resulting in a slight negative activation energy. Singleton and Cvetanovic<sup>2</sup> explained the occurrence of these negative activation energies in apparently elementary, high pressure limit, gas-phase reactions as being due to the formation of a loosely bound prereactive complex that is formed without activation energy, followed by a second reaction whose transition state energy is lower than the energy of the separated reactants. For systems at low pressure, Mozurkewich and Benson<sup>3</sup> used the Rice-Ramsperger-Kassel-Marcus theory to develop quantitative expressions for the rates of reactions that have negative activation energies and highly curved Arrhenius plots. They postulated a typical reaction profile presenting a minimum, corresponding to the formation of a stable intermediate complex in between two transition states, the first one loose and the second one tight. The tight transition state should have a significant threshold energy with respect to the intermediate but may have a negative potential energy relative to the reactants. The applications to the reactions of OH with CO, HNO<sub>3</sub>, and HNO<sub>4</sub> are consistent with such a profile.<sup>4</sup>

Rate constants for the OH attack on a large variety of hydrocarbons have been measured and reported.<sup>5</sup> However, the regioselectivity of the OH addition is usually not specified, because rates are given for the global consumption of OH radicals. Also, because these reactions occur with a very small activation energy, they depend on other molecules for the stabilization of the adduct and they are very sensitive to experimental conditions, in particular to pressure. Thus, detailed mechanisms are not well known. Theoretical work has only been reported for ethylene and acetylene, and only for the initial OH attack.<sup>6</sup> Yet, because so many experimental data are available, they constitute an ideal subject for the theoretical study of radical additions to a  $\pi$  bond and to try and understand the subtle interactions governing radical attack in general.<sup>7</sup>

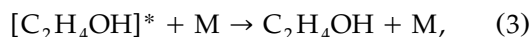
Among alkenes, propene is especially important in the troposphere of large cities because of its very high ozone-forming index.<sup>8</sup> In addition, because it is the simplest unsaturated system exhibiting the possibility of a differential selectivity for OH addition, it is interesting to study the detailed mechanism of reaction (1) when R is propene. Experimental results are not conclusive on whether the addition of OH to propene occurs at the terminal or at the central carbon atom. On the basis of the analysis of the final products after O<sub>2</sub> addition

in an NO<sub>x</sub> free atmosphere, Cvetanovic<sup>9</sup> reported that 65% of the additions occur at the terminal carbon atom. Yet, simple thermochemical considerations suggest that the central atom OH-propene adduct is the most stable one.<sup>10</sup> In a previous theoretical study of the propene-OH-O<sub>2</sub> reaction,<sup>10</sup> we gave a possible explanation for the above discrepancy, based on the calculation of the reaction paths along both addition channels for the two consecutive reactions corresponding to the addition of OH and molecular oxygen. Results showed that, although the first step indeed favors the addition of OH to the central carbon atom of propene, the subsequent reaction with O<sub>2</sub> has a significantly lower transition state when O<sub>2</sub> is added to the terminal OH adduct, thus providing a crossing between the two reaction paths that can explain the final results obtained in ref. 9.

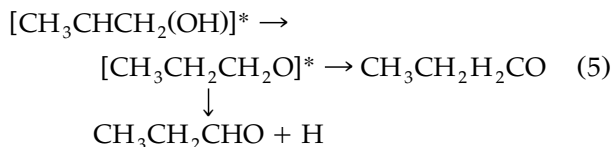
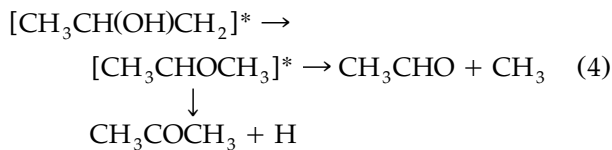
If the same reaction occurs in an inert atmosphere and at low pressure, the excited adduct [R—OH]\* cannot be stabilized by collisions, and Bartels et al.<sup>11</sup> proposed that for ethene a rearrangement takes place followed by decomposition, according to the following reaction:



At 295 K and 2.7 mbar (He), the total yield of reactions (2) is found to be 4 times the yield of the stabilized adduct,



suggesting that these channels are relevant in consuming OH at low pressures. For propene in analogous conditions, one expects each  $\beta$ -hydroxyalkyl radical, [R—OH]\*, to yield a different alkoxy radical, [RH—O]\*, which would decompose into different carbonyl compounds and radicals:



In this work, reactions (2), (4), and (5) will be studied by means of *ab initio* calculations in order to (i) verify the theoretical feasibility in the

propene-OH system of a rearrangement similar to the one proposed by Bartels et al.<sup>11</sup> for ethene-OH, (ii) reproduce and explain the observed negative activation energies in alkene-OH additions, and (iii) determine the regioselectivity of the OH addition to propene in conditions such that no other bimolecular reactions may affect the observations. Structures and energetics of the reactants,  $\pi$  complexes, products, and transition states for the rearrangement and subsequent decomposition of the OH-propene adducts in the absence of molecular oxygen and at low pressures will be obtained, and the corresponding reaction paths will be followed in detail. The OH + ethene system will also be calculated for comparison, because experimental data are available for this system at low pressure in an inert atmosphere.<sup>13</sup> The contribution of the entropy factor to the selectivity will be discussed.

## Computational Methodology

Electronic structure calculations were performed with the Gaussian 94 (G94) system of programs.<sup>14</sup> Restricted Hartree-Fock theory (RHF) was used for closed shell systems, and unrestricted Hartree-Fock theory (UHF) was used for open shell systems (radicals). The correlation energy corrections were introduced with Møller-Plesset perturbation theory up to fourth order (MP4 and UMP4 for closed and open shell systems, respectively). Results from spin projected calculations were used (PMP4), because it has been shown<sup>6,15</sup> that they yield energy differences that are in far better agreement with experimental values.

All geometries were fully optimized at the MP2/6-31G\*\* and MP2/6-311G\*\* levels, and the character of the transition states was confirmed by frequency calculations presenting one and only one imaginary frequency. Single point MP4 (SDTQ) energy calculations were performed with the 6-31G\*\* basis for reactants, transition state, and products at the MP2-optimized geometries. Again, the projected results (PMP4) were used. Single point QCI(SD) of the  $\beta$ -hydroxyalkyl radicals were also performed with the 6-31G\*\* basis set to verify that no changes were observed in the selectivity. The zero point energies (ZPE) were obtained from frequency calculations at the MP2/6-311G\*\* level.

The *ab initio* calculations were performed in part on the Cray YMP4/464 and on the Silicon

Graphics Origin 2000 at the Universidad Nacional Autónoma de México (UNAM), and in part on the Silicon Graphics Power Challenge at the Universidad Autónoma Metropolitana-Iztapalapa (UAM-I) in Mexico City.

## Results and Discussion

The optimized geometries of all the relevant points along the reaction path for the addition of OH to propene at the terminal and central carbon atoms, for the subsequent migration of the hydrogen atom, and for the final decomposition reaction were obtained at the MP2 level with two different basis sets, the 6-31G\*\* and 6-311G\*\*. New calculations on the ethene + OH system were performed with the larger triple-zeta basis for comparison. Because the structures of the prereactive stable intermediates and the transition states (TS1) for the reaction OH + propene for addition at the central and terminal C atoms were reported in previous work,<sup>10</sup> they are not given here, although they are included in the discussion. The transition states (TS2) for the hydrogen atom migration in an inert atmosphere at low pressure for the ethene-OH system and after addition of OH at the two carbon atoms in propene are represented in Figure 1. The relevant lengths and angles for the bonds that are broken and formed during the migration reaction are indicated on the figures, as obtained in the calculation using the triple-zeta basis set. It can be seen that the three transition states in Figure 1 are definitely "tight" transition states, corresponding to strained structures, with a CCH angle of only about 80.7° and a CCO angle less than 90°. Also, the distances between the migrating hydrogen atom and the atoms to which it is connected are only about 0.3 Å larger than the normal bond lengths, and the proton was closer to its final position after migration. These distances may be compared with the corresponding ones in TS1,<sup>10</sup> which is a characteristically "loose" transition state where the C...O distance is more than 0.6 Å longer than for a normal C—O bond.

All energy results are given in Table I in hartrees and correspond to spin-projected values. The average values of the square of the total spin angular momentum,  $\langle S^2 \rangle$ , are reported in Table II before and after annihilation of the quartet terms. It can be seen that the values of  $\langle S^2 \rangle$  for the first transition states are somewhat larger (0.95) than the 0.75 value for a doublet state, but this is well corrected

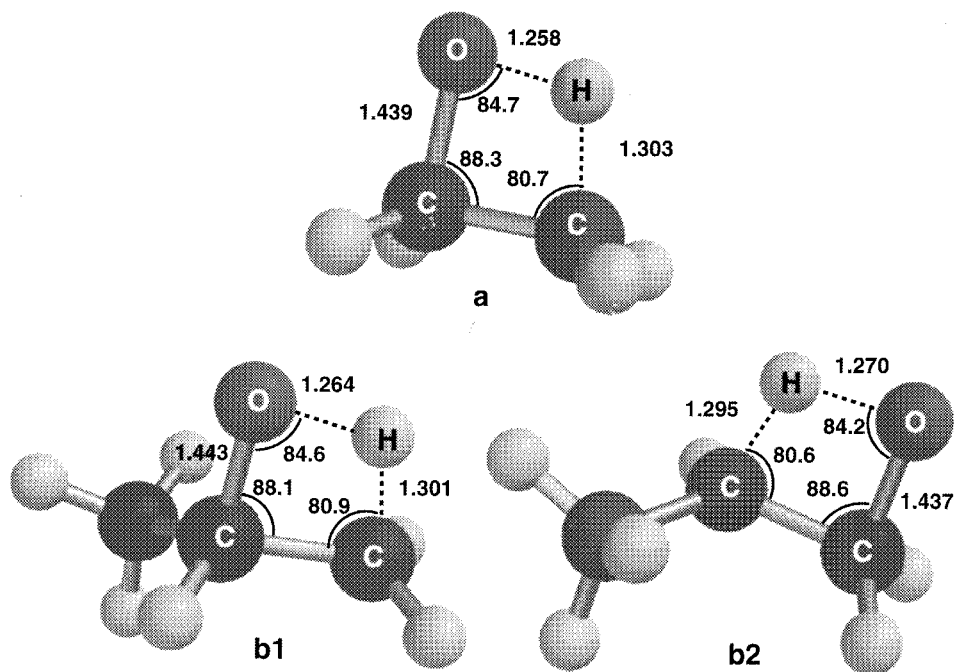


FIGURE 1. Transition states for the proton migration in (a) ethene-OH and (b) propene-OH.

by projection. Spin contamination of all stable intermediates and the rearrangement transition states is negligible. The energy results obtained from a single point PMP4(SDTQ) calculation performed at the MP2 geometry are also given in Table I. The corresponding  $\langle S^2 \rangle$  values are very similar to those obtained at the MP2 level. Table I also contains QCI(SD) results obtained at the MP2/6-311G\*\* optimized geometries for the  $\beta$ -hydroxyalkyl radicals. Table III contains the relative energies (kcal/mol) calculated with respect to the energy of the isolated reactants, and including the zero point vibrational energy correction. In Table III, data for the ethylene + OH reaction at the MP2/6-311G\*\* level are also reported. The ZPE used in this table are those obtained in the MP2 calculations.

The magnitude of the basis set superposition error (BSSE) was estimated first at the MP2/6-311G\*\* level using the counterpoise method.<sup>16</sup> However, this method is known to provide only a crude estimate and not an upper bound on the error;<sup>17,18</sup> indeed, the results obtained here do not appear to be reliable. Although the contributions to the propene and ethene energy due to the presence of the basis functions on the OH radical are approximately the same (0.94 and 0.81 kcal/mol, respectively), the contributions of the propene and ethene basis functions to the OH radical energy are

abnormally different (1.33 and 0.22 kcal/mol, respectively), yielding total BSSEs of 2.27 kcal/mol for the propene-OH system and 1.03 kcal/mol for ethene-OH. Several authors recommended that, because the BSSE decreases as the basis set increases, a larger basis set should be used rather than introduce a doubtful correction. In this work the energy profiles were recalculated with the triple-zeta 6-311G\*\* basis set: the energy differences were found to be practically the same.

Figure 2 shows the PMP2 energy profiles along the reaction paths for the whole OH-propene-products process and for addition of OH on the central carbon atom (solid line) and on the terminal one (dotted line). Energies are given in kilocalories/mole relative to the free reactants and include the ZPE corrections. Because geometries are optimized with respect to the value of the unprojected energy, the PMP2 minimum could be shifted with respect to the MP2 one. This possibility was checked out, but complete agreement was found in all cases. In the limit of low pressure, the prereactive  $\pi$  complex that was formed at the beginning of the reaction and whose total energy corresponds to the first shallow minimum in Figure 2 is expected to preserve its excess kinetic energy instead of stabilizing through collisions. Thus, its lifetime must be so small that, in these

**TABLE I:**  
Total Energies (hartrees) of Reactants, Stable Intermediates, Transition States, and Products in OH-Propene Reaction.

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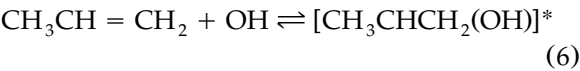
conditions, it becomes irrelevant and will not be considered further. Previous results<sup>10</sup> indicate that the energy barriers TS1 are very similar for the two channels, the barrier for the addition at the central carbon being about 0.35 kcal/mol lower than at the terminal one. If the activation entropies are considered (as calculated in Gaussian 94), one finds that the central carbon transition state has

TABLE II.  
S<sup>2</sup> Values for OH + Propene Reaction at  
MP2/6-311G\*\* Level.

System	S <sup>2</sup> before projection	S <sup>2</sup> after projection
Isolated reactants	0.7552	0.7500
Prereactive $\pi$ complex	0.7553	0.7500
Transition state I		
Terminal C	0.9506	0.7551
Central C	0.9450	0.7549
$\beta$ -Hydroxyalkyl radicals		
Terminal C	0.7632	0.7501
Central C	0.7617	0.7501
Transition State II		
Terminal C	0.7912	0.7506
Central C	0.7914	0.7506
Alkoxy radicals		
Terminal C	0.7632	0.7501
Central C	0.7577	0.7500
Products	0.7608	0.7501

1.04 cal/mol K less entropy than the terminal. At 300 K, this difference is equivalent to 0.3 kcal/mol, which cancels the energy difference and yields practically the same activation free energy for both. However, a difference of about 2 kcal is observed between the calculated energies of the two  $\beta$ -hydroxyalkyl radicals (Table III), suggesting a preference for the OH addition to occur at the central carbon atom of propene. Almost the same energy difference between the  $\beta$ -hydroxyalkyl radicals was obtained when the calculations were performed with QCI(SD) and a 6-31G\*\* basis set at the MP2 optimized geometry.

After the formation of the  $\beta$ -hydroxypropyl radical, two reactions are then possible in the absence of collisional stabilization: the dissociation back to reactants (with a reaction rate constant  $k_{-1}$ ) and a protonic migration to form an alkoxy radical (reaction rate constant  $k_2$ ). The latter, however, presents a very high energy transition state of more than 30 kcal/mol with respect to any of the  $\beta$ -hydroxypropyl radicals. Thus, at low pressures and in an inert atmosphere, the reaction



becomes reversible. However, because the energy of the TS2 is only slightly higher (by 1.32 kcal/mol) than the energy of the initial reactants (Table II), at

TABLE III.  
Energy Values (kcal / mol) Relative to Isolated Reactants for Propene and Ethene Reactions.

System	Method				
	PMP2 / 6-311G**			PMP4 / 6-311 + G** // MP2 / 6-311G**	
	C <sub>2</sub> H <sub>4</sub> + OH	C <sub>3</sub> H <sub>6</sub> + OH (terminal C)	C <sub>3</sub> H <sub>6</sub> + OH (central C)	C <sub>3</sub> H <sub>6</sub> + OH (terminal C)	C <sub>3</sub> H <sub>6</sub> + OH (central C)
Isolated reactants	0.0	0.0	0.0	0.0	0.0
Prereactive $\pi$ complex	-3.2 (-0.9)	-4.4 (-2.9)	-4.4 (-2.9)	-3.2 (-1.8)	-3.2 (-1.8)
Transition state I	-1.1 (-0.9)	-1.7 (0.8)	-2.1 (0.4)	-2.1 (0.4)	-2.2 (0.3)
$\beta$ -Hydroxyalkyl radicals	-30.2 [-29.5] (-26.4)	-30.5 (-26.9)	-33.2 (-28.8)	-27.4 (-23.8)	-29.7 (-25.3)
Transition state II	3.6 [ $\leq 2$ ] (5.53)	3.9 (5.9)	1.3 (2.5)	5.7 (7.7)	3.4 (5.0)
Alkoxy radicals	-27.2 [-25.9] (-23.4)	-32.5 (-28.0)	-27.3 (-23.3)	-29.0 (-24.5)	-26.9 (-22.5)

The numbers in brackets are the experimental values proposed by Bartels et al.<sup>11</sup> The values in parentheses are the relative energies including the ZPE corrections at the MP2/6-311G\*\* level.

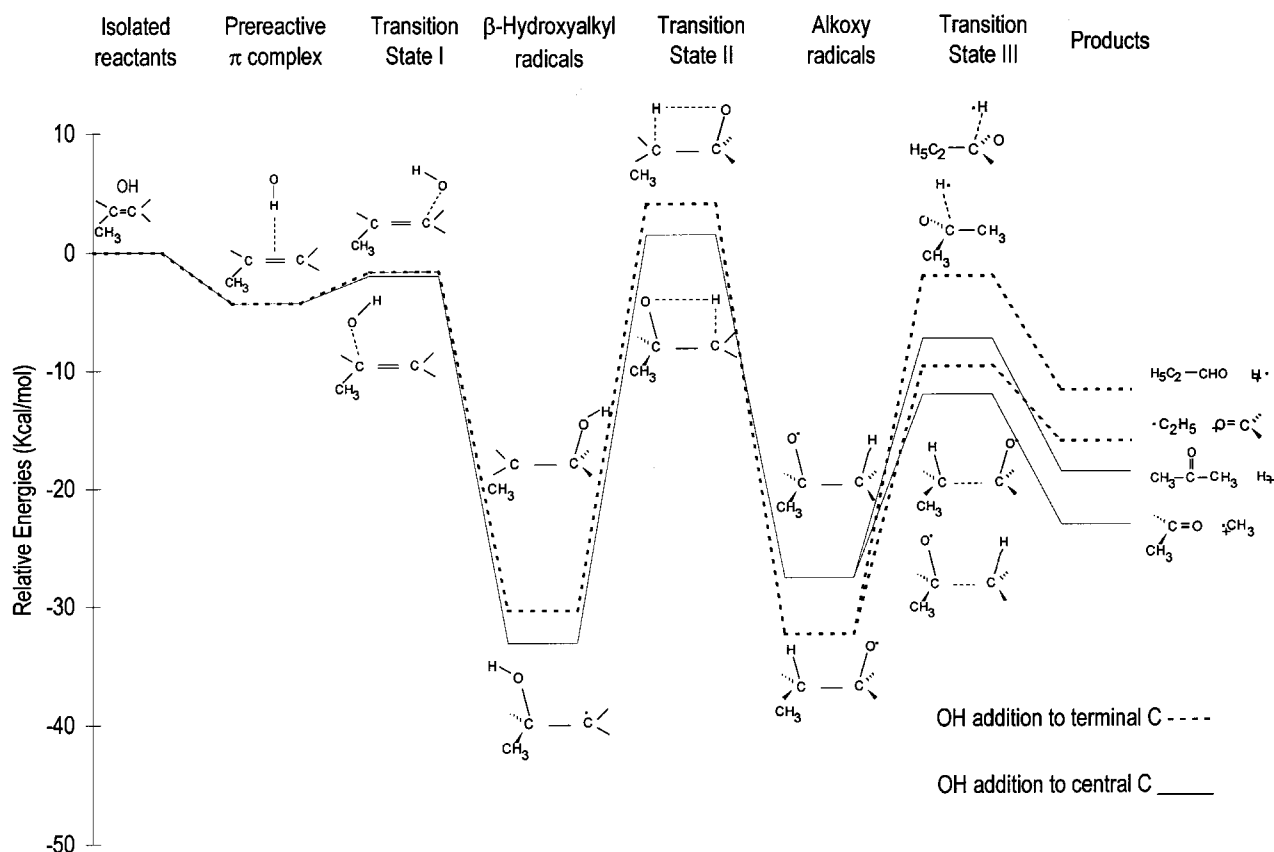


FIGURE 2. Energy profiles for the OH + propene reaction, for addition at the terminal and at the central carbon atoms.

sufficiently low pressures a small fraction of the radicals may proceed to form the alkoxy radicals. Once these intermediates are formed, the dissociation reactions are expected to be fast (because the energy barrier TS3 is much smaller than TS2) and irreversible, the reverse bimolecular reaction being improbable at such low pressures.

Four different sets of final products can be obtained in principle, the most stable ones being acetaldehyde and a methyl radical derived from the original OH addition to the central carbon atom. A quantitative characterization of these final products could provide a definitive answer to the regioselectivity in the OH addition to propene.

The energy profile shown in Figure 2 is typical of the cases studied by Mozurkewich et al. [3, 4] of reactions exhibiting negative activation energies that occur in two steps: a reversible step with a loose transition state to form the addition complex; and a tight transition state, corresponding to the proton migration. If the temperature increases, so does the possibility of both the reverse reaction and the rearrangement reaction. But, because the first transition state is loose, a temperature in-

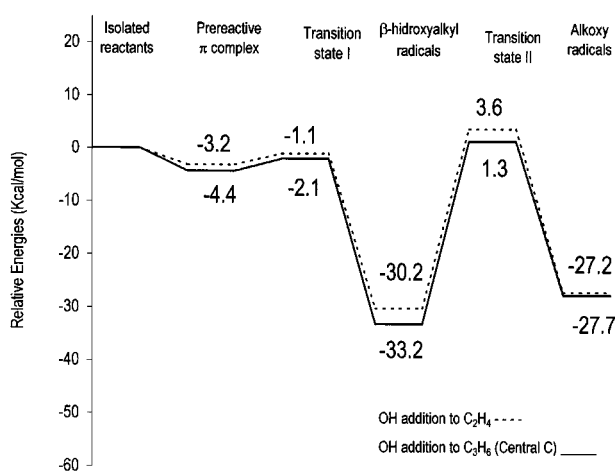


FIGURE 3. Comparison of the energy profiles for the OH + propene and OH + ethene reactions.

crease favors the reverse reaction and thus decreases the OH consumption rate. In terms of the Arrhenius equation, this implies a negative activation energy.

Figure 3 compares the partial reaction path for ethene + OH with the one for propene + OH.

Bartels et al.<sup>11</sup> estimated that for the ethene + OH reaction, the difference in energies between the first and second transition states should be about 2 kcal/mol, which agrees reasonably well with the value of 3.6 kcal/mol obtained in this work. This difference is a measure of the ratio  $k_{-1}/k_2$  (i.e., of the relative importance of the reverse reaction as compared with the rearrangement reaction). For propene, for the intermediate with OH added at the central carbon atom, we obtain 1.32 kcal/mol, suggesting that the forward reaction could be more favorable in propene than in ethene, yielding an effective rate constant for OH consumption that is larger for propene than for ethene.

## Conclusions

We report calculations performed on a reaction involving a radical-molecule process and characterized by having an apparently close to zero negative activation energy. Structures and energies were obtained at the MP2/6-31G\*\* and MP2/6-311G\*\* levels, and single point MP4(SDTQ) energies were calculated for reactants, stable intermediates, transition states, and products for the reaction initiated by the attack of OH on propene in an inert atmosphere. Even though the results at the higher level are expected to be quantitatively more exact, the projected energy results obtained with the smaller basis set and the MP2 method are adequate to describe the mechanism of the reaction, and we suggest that they could be used in similar reactions. Results for the OH + ethene reaction are also obtained, and they are included in our analysis.

Different external conditions are considered: very low pressure, when collisional stabilization of intermediates does not occur; and normal pressures, when such stabilization is possible.

The attack of an OH radical to the C=C double bond at the more substituted carbon atom was found to have a slightly smaller activation energy; also, from the point of view of the entropy, the more substituted carbon atom was the favored position for the attack. However, these differences are so small that one can expect that some subsequent reaction should, in fact, be responsible for the observed selectivity. The regioselectivity of the OH addition to propene was discussed in previous work.<sup>10</sup> On the basis of *ab initio* calculations, it was shown that addition occurred preferentially on the central carbon atom, even though in an O<sub>2</sub>

atmosphere a subsequent reaction favored the products obtained after addition of OH at the terminal C atom. In the case studied in this work in an inert atmosphere, the second step presents no inversion and the addition at the central carbon atom should be the preferred channel. As the pressure increases collisional stabilization starts to compete, and it should be possible to isolate both  $\beta$ -hydroxypropyl radicals.

The model proposed by Mozurkewich and Benson<sup>3</sup> to account for observed negative activation energies (i.e., a decrease in rate constants on increasing temperature) is well suited to describe reactions at low pressures such as the ones studied in this work. The existence of a prereactive stable complex followed by a transition state that has a lower energy than the reactants explains, according to the mechanism postulated by Singleton and Cvetanovic,<sup>2</sup> the negative activation energies at high pressures.

The good correspondence obtained between the *ab initio* calculated energies and the experimental results allows us to conclude that the energy variation is probably the decisive factor in the course of reactions of the OH radical with alkenes. Energy profiles are being calculated for the reaction of a series of other small alkenes with the OH radical to obtain a correlation between the difference in energy between the two transition states and the observed negative activation energies.

## Acknowledgments

The authors gratefully acknowledge financial support from Instituto Mexicano del Petróleo through program FIES-95-97-VI. We wish to thank Dr. R. Atkinson for valuable discussions and suggestions. One of us (J.R.A.I.) wishes to thank the Third World Academy of Sciences for travel support within the framework of the TWAS South-South Fellowship Programme.

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